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CHEMICALLY MODIFIED CARBON ELECTRODES. XVII. METALLATION OF IMM--ETC(U)  
MAR 79 R D ROCKLIN, R W MURRAY    N00014-76-C-0817

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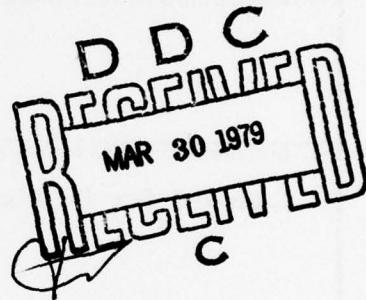
## TECHNICAL REPORT NO. 9

CHEMICALLY MODIFIED CARBON ELECTRODES XVII. METALLATION OF IMMOBILIZED  
TETRA(AMINOPHENYL)PORPHYRIN WITH MANGANESE, IRON, NICKEL, COPPER AND  
ZINC, AND ELECTROCHEMISTRY OF DIPROTONATED TETRA(PHENYL)PORPHYRIN

by

Roy D. Rocklin and Royce W. Murray

Prepared for Publication in the  
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(6) CHEMICALLY MODIFIED CARBON ELECTRODES. VII. METALLATION OF IMMOBILIZED TETRA(AMINOPHENYL)PORPHYRIN WITH MANGANESE, IRON, NICKEL, COPPER AND ZINC, AND ELECTROCHEMISTRY OF DIPROTONATED TETRA-PHENYL-PORPHYRIN.

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#### ABSTRACT

Tetra(aminophenyl)porphyrin can be amide-bonded to oxidized glassy carbon surfaces following activation with acetyl chloride or thionyl chloride, with the latter affording higher coverage. The immobilized porphyrin can be metallated with manganese, iron, cobalt, nickel, copper and zinc. The metalloporphyrins undergo electrochemical reactions in DMSO solvent at metal and ring-centered reduction potentials expected on the basis of solution molecular analogs. In the case of iron-metallated porphyrin, electrochemistry can be done in aqueous acid, where a clear but porphyrin-debilitating dioxygen catalysis is observable. A small reverse wave at ca. 0.4 volt vs. NaSCE in  $\text{CH}_3\text{CN}$  and DMSO solvent is interpreted as reoxidation of diprotonated surface bound porphyrin.

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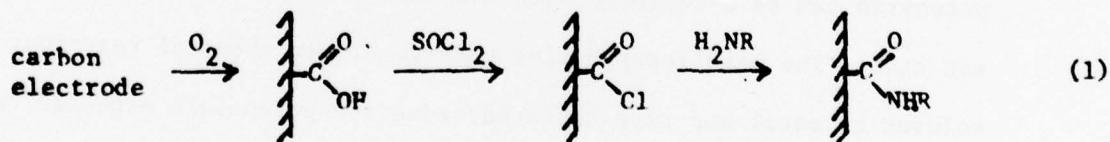
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INTRODUCTION

In previous papers<sup>1,2</sup> we showed that reaction sequence 1 could be used to bind tetra(p-aminophenyl)porphyrin, designated  $T(p\text{-NH}_2)\text{PP}$ , to the surface of glassy (vitreous) carbon electrodes.



The immobilized porphyrin and its in situ cobalt metallated daughter exhibit reversible surface electrochemical waves with formal potentials similar to those of the solution dissolved analogs<sup>3</sup>.

The favorable properties of the carbon-porphyrin electrodes invite exploitation of the rich porphyrin and metalloporphyrin chemistry and electrochemistry. In this paper, we report the in situ metallation and subsequent electrochemistry of carbon bound  $T(p\text{-NH}_2)\text{PP}$  with manganese, iron, nickel, copper, and zinc, including the electrocatalytic reduction of dioxygen using the iron-metallated surface. We have also continued

investigation of the nature of the bonding of the porphyrin to the carbon surface and describe an alternate attachment procedure. Finally, we will present the results of an investigation of the electrochemistry of solution dissolved diprotonated tetraphenylporphyrin,  $H_2TPP^{2+}$ , and its connection to previous observations for surface porphyrin<sup>2</sup>. The dissolved  $H_2TPP^{2+}$  species exhibits a very low reduction potential.

#### EXPERIMENTAL

Tetra(p-aminophenyl)porphyrin,  $T(p-NH_2)PP$ , was prepared as described earlier<sup>1,4</sup>. Further purification of the porphyrin, by chromatography on a short silica gel column with 1%  $CH_3OH$  and 99%  $CHCl_3$  (V/V), resulted in increased coverage on the electrode surface and lower carbon electrode background currents than in the early experiments. Tetraphenylporphyrin was synthesized by the method of Adler, *et al.*<sup>5</sup> Glassy carbon rod (Atomergic Chemetals Corp., Plainview, N.Y., Grade V10-50, 2.6 mm diameter) cut into electrodes ~4 mm long was polished on the cylinder end with successively finer alumina polishing compound, finishing with 1 $\mu$  diamond paste. The polished electrodes were then oxidized in an RF plasma<sup>6</sup> for 30 minutes at 200 mtorr of  $O_2$  and ca. 5 watts. There was no noticeable difference between electrodes oxidized in the RF plasma and those oxidized by baking in  $O_2$  at 450°C, as in our earlier procedure.

The oxidized electrodes were refluxed with ca. 2 ml freshly distilled  $SOCl_2$  in ca. 15 ml  $Na^0$  dried toluene. After one hour, the electrodes were removed, briefly rinsed in dry toluene, and placed in a refluxing solution<sup>7</sup> of < 1 mg  $T(p-NH_2)PP$  in 15 ml dry toluene for 2.5 hours. Following reaction, the electrodes were rinsed with toluene and then copiously with methanol and dimethylformamide (DMF), which are effective at removing any adsorbed porphyrin, and air dried. The procedure for activating the

oxidized carbon surface with acetyl chloride is the same, except thionyl chloride is replaced with acetyl chloride.

In this work, the porphyrin was metallated after it had been bound to the carbon surface<sup>8</sup>. This procedure has the advantage of consuming very little porphyrin reagent, and further insures removal of any adsorbed material. Cobalt, nickel, copper, and zinc were inserted by refluxing the carbon-T(p-NH<sub>2</sub>)PP electrode in a DMF solution of their metal(II) chlorides for 15 minutes<sup>9</sup>. For manganese metallation, manganese(II) acetate was employed instead of the chloride, and the DMF solvent was carefully degassed to avoid MnO<sub>2</sub> formation. We were not successful at inserting iron by the usual refluxing DMF procedure without detaching or otherwise incapacitating the porphyrin, but the method of Collman, et al.<sup>10</sup> proved suitable. The carbon-porphyrin electrodes were refluxed in tetrahydrofuran (Aldrich, 99.9%, water content <0.006%, or freshly distilled from LiAlH<sub>4</sub>) solution of anhydrous FeCl<sub>2</sub> for three to six hours.

A conventional non-aqueous cell with Luggin (NaSCE) reference electrode was employed for electrochemical experiments. A PAR Model 174 served as potentiostat and a locally designed<sup>11</sup> triangular wave generator as signal source. Phase selective AC voltammetry experiments<sup>2</sup> employed a PAR HR-8 lock-in amplifier. XPEIS spectra were obtained on a DuPont 650B Electron Spectrometer with Mg anode. Dimethylsulfoxide (DMSO) and benzonitrile solvents were dried over Linde 4A molecular sieves and contained 0.1 M Et<sub>4</sub>N<sup>+</sup>ClO<sub>4</sub><sup>-</sup> supporting electrolyte.

#### RESULTS AND DISCUSSION

Bonding of T(p-NH<sub>2</sub>)PP to Oxidized Carbon Electrodes. In our previous papers<sup>1,2</sup> we described experiments designed to elucidate the manner in which the tetra(p-aminophenyl)porphyrin is bonded to the carbon electrode

surface. An XPES analysis for uncoupled amine<sup>2</sup> on the porphyrin surfaces showed that on the average two of the four amine groups of the T(p-NH<sub>2</sub>)PP remained uncoupled after the surface bonding. We have continued to probe the details of bonding and describe here results of some additional experiments.

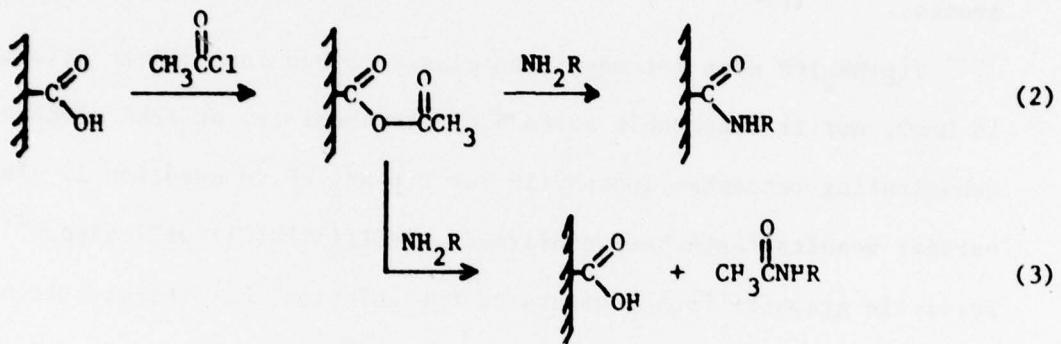
T(p-NH<sub>2</sub>)PP does not adsorb on glassy carbon from dilute solutions in DMSO, nor is detectable surface electrochemistry or XPES produced by substituting tetraphenylporphyrin for T(p-NH<sub>2</sub>)PP in Reaction 1. These earlier results<sup>1</sup> have been confirmed. Fe(III)TPP(Cl) will adsorb<sup>12</sup> on pyrolytic graphite from a saturated DMF solution, but the electrochemical detection of this adsorption, done in a medium in which no dissolved porphyrin is present, requires use of a solvent (water) in which the porphyrin is poorly soluble.

We believe it is safe to claim that the interaction of T(p-NH<sub>2</sub>)PP with the glassy carbon surface under the reaction conditions employed depends on the presence of the amine function and its role in covalent amide bond formation as opposed to adsorptive effects.

Koval and Anson have reported<sup>13</sup> that oxidized but not (thionyl chloride) activated pyrolytic graphite strongly binds aminomethylpyridine. We have made similar observations for glassy carbon, which after oxidation but without thionyl chloride treatment binds aminophenylferrocene<sup>14</sup> and as established during this study, T(p-NH<sub>2</sub>)PP. The coverage in the latter case (Table I, Entry 3), is small but the electrochemical potentials, stability, and general behavior are otherwise quite similar to results obtained (Entry 1) using thionyl chloride activation. This binding does not occur with non-amine-bearing reagents, and may be associated with reactive acid anhydride groups on the carbon surface.

This would produce amide bonding just as effectively as Reaction 1, of course.

Acetyl chloride, substituted for thionyl chloride, should form surface anhydrides reactive with  $T(p\text{-NH}_2)\text{PP}$ .



Entry 2, Table 1, shows that this procedure does result in binding of  $T(p\text{-NH}_2)\text{PP}$ . Electrochemical properties are again indistinguishable from thionyl chloride activated reactions except the attained coverage is lower (compare Entries 1, 2), but on the other hand much higher than that attained in the absence of activating reagent (Entry 3). The difference in coverage between acetyl and thionyl chloride activated electrodes is explicable from the non-productive path of Reaction 3, which surely competes with Reaction 2.

Our earlier XPES-based analysis of two uncoupled amine functions per average  $T(p\text{-NH}_2)\text{PP}$  bound to carbon has been confirmed by R. Nowak in this laboratory<sup>14</sup>. This result was taken to indicate<sup>2</sup> an average of two amide bonds between the  $T(p\text{-NH}_2)\text{PP}$  and carboxylic sites on the carbon surface.  $T(p\text{-NH}_2)\text{PP}$  doubly linked to the surface could be bonded either  $\alpha,\beta$  ("edge on"), or  $\alpha,\gamma$  ("face down"). Approximating the porphyrin molecule as a  $12\text{ \AA} \times 12\text{ \AA} \times 4\text{ \AA}$  volume, about  $1.2 \times 10^{-10}$  mole/cm<sup>2</sup> could lie face down on a flat surface and  $3.5 \times 10^{-10}$  mole/cm<sup>2</sup> edge on. The highest

attained experimental coverage of  $T(p\text{-NH}_2)\text{PP}$ ,  $1.4 \times 10^{-9}$  mole/cm<sup>2</sup>, would require a surface roughness factor of 4X, a reasonable number. Even after considerable polishing of our glassy carbon electrodes, the surface still, sometimes visibly, exhibits pores and other defects. Different brands and samples of glassy carbon probably possess widely varying surface roughness factors.

A high coverage such as  $1.4 \times 10^{-9}$  mole/cm<sup>2</sup> could alternatively be interpreted as evidence for multilayer coverage, where dissolved  $T(p\text{-NH}_2)\text{PP}$  molecules for instance are activated by residual  $\text{SOCl}_2$  and couple with amine sites of surface amide-bonded porphyrin, forming sulfimide bonds:  
$$\text{porphyrin-NH-S}^0\text{-NH-porphyrin}$$
. However, S 2p bands cannot be detected by XPS on our highest coverage porphyrin electrodes, so if multilayers are forming, some other and as yet unknown linking mechanism must be involved.

Electrochemistry of Unmetallated Carbon  $T(p\text{-NH}_2)\text{PP}$  Electrodes. A cyclic voltammogram of immobilized but not metallated  $T(p\text{-NH}_2)\text{PP}$  is shown in Figure 1 to illustrate the considerable improvement in wave definition since the previous reports<sup>1,2</sup>. The carbon electrode background current is smaller, and the charge under the porphyrin reduction peaks is larger. The increased purity of the  $T(p\text{-NH}_2)\text{PP}$  appears to permit longer reaction times without surface contamination by impurities, which raise the background current level. Table I summarizes data (Entry 1) for the unmetallated carbon- $T(p\text{-NH}_2)\text{PP}$  electrodes. The formal potentials measured in DMSO solvent agree with those measured previously<sup>1,2</sup> and with literature values<sup>3</sup>. As before, surface coverage varies widely from sample to sample, but on a given electrode the charge under the four peaks shown in Figure 1

is roughly equal. We have found the splitting between the cathodic and anodic peak potentials ( $\Delta E_p$ ) is essentially zero for both ring reductions of immobilized  $T(p\text{-NH}_2)\text{PP}$ , and for ring reductions in metallated porphyrins, when the surface coverage is high as in Figure 1. Electrodes exhibiting lower porphyrin coverage tend to exhibit measurable  $\Delta E_p$  values.

The more negative member of the "waves II" doublet observed previously<sup>2</sup> for  $T(m\text{-NH}_2)\text{PP}$  on carbon is perceptible at ca. -1.75 volt. Its intensity relative to the main wave is smaller than in the earlier data.

Electrochemistry of Metallated Carbon  $T(p\text{-NH}_2)\text{PP}$  Electrodes. An appealing feature of immobilized  $T(p\text{-NH}_2)\text{PP}$  is that it can be metallated in situ without cleaving the amide bonds binding the porphyrin to the carbon surface. Procedures suitable for metallation in conventional solutions prove suitable for in situ surface metallations, except for iron where the usual DMF reaction medium was replaced with a known<sup>10</sup> alternative (THF). We have not been successful using the in situ approach with second row transition metals, however. For example, an attempt to prepare the ruthenium porphyrin by refluxing a  $T(p\text{-NH}_2)\text{PP}$  electrode with a decalin solution of  $\text{Ru}_3(\text{CO})_{12}$  destroyed the surface structure. Preparation of the appropriate amino-metallocporphyrin will probably be necessary to deal with such cases.

AC voltammetry of electrodes metallated by DMF reflux with the chlorides of  $\text{Ni(II)}$ ,  $\text{Cu(II)}$ , and  $\text{Zn(II)}$  is illustrated in Figure 2b. Cyclic voltammetry of the  $\text{Cu(II)}$  complex is shown in Figure 2a; those of the other metallocporphyrins have comparable definition. These metallocpor-

phyrins are similar in that the pair of reductions corresponds to porphyrin ring reductions<sup>15</sup>. The formal potentials for the three metallocporphyrins, listed in Table I (Entries 5, 7, 8) are in reasonable agreement with solution data. The solution analogs employed are the corresponding metalloc tetraphenylporphyrins, which because of the absence of the electron donating amino substituent<sup>16</sup> should be slightly easier to reduce. This may be the source of the small but consistent ca. 40-60 mv. negative shift of the surface metallocporphyrin potentials as compared to the solution tetraphenylporphyrin ones. (A similar small potential difference is noticeable for the unmetallated porphyrin, Entry 1).

Previous experiments in the non-coordinating solvent  $\text{CH}_2\text{Cl}_2$  with cobalt, nickel, and zinc tetraphenylporphyrins report no influence of added ligands on the porphyrin reduction potentials<sup>18</sup>. In agreement with this, the surface waves for these three metallocporphyrins are perturbed only slightly by addition of a neutral base such as pyridine using DMSO as solvent.

Figure 2b shows a third peak for the carbon  $\text{ZnT}(\text{p-NH}_2)\text{PP}$  surface at ca. -1.93 volt vs. NaSCE. This peak is seen only at slow scan rates in AC voltammetry; at a 10 mv/sec. scan rate it is substantially smaller, and is completely absent in DC cyclic voltammetry at 100 mv/sec. scan rate. This behavior suggests a slow chemical conversion after the first two ring reductions to generate a third electroactive state. Wilson, et al.<sup>19</sup> in studies of zinc tetraphenylporphyrin in DMF have also observed a wave more negative than the second ring reduction and have attributed it to the product of slow protonation of the zinc tetraphenylporphyrin dianion.

Metallation of the carbon- $\text{T}(\text{p-NH}_2)\text{PP}$  surface with copper proved so facile that the trace copper resulting from corrosion of a brass electrode

holder in contact with DMSO solvent would metallate the electrode within about two days. A cyclic voltammogram of an electrode prepared in this way is shown in Figure 2a. Both waves are shifted positively 50 mv relative to the conventionally-metallated electrode; the reason for this repeatable potential shift is unknown.

The carbon bound manganese, iron and cobalt  $T(p\text{-NH}_2)_2\text{PP}$  exhibit changes in the metal oxidation state, as well as ring reductions. Table 1 lists formal potentials for these metalloporphyrins in DMSO (Entries 4, 9, 10). These immobilized metalloporphyrins are particularly interesting due to the chemistry of the metal's axial positions. Molecular oxygen takes the sixth position of five-coordinate Fe(II) porphyrin in hemoglobin. Several metalloporphyrin dioxygen carriers have been synthesized, notably Collman's picket fence porphyrins<sup>10</sup>, and including other metalloporphyrins of Cr<sup>20</sup>, Mn<sup>21</sup>, and Fe<sup>22</sup>.  $\mu$ -oxo dimer formation is part of the axial chemistry of the Mn<sup>23</sup> and Fe<sup>10,24</sup> porphyrins. The electrochemical potentials of the central metal are sensitive to the axial ligation. This sensitivity has been demonstrated<sup>2</sup> for the surface bound  $\text{CoT}(\underline{m}\text{-NH}_2)_2\text{PP}$ , and we have established an analogous sensitivity for cobalt and iron-metallated carbon- $T(p\text{-NH}_2)_2\text{PP}$  electrodes. Quantitative features of axial coordination chemistry for these surfaces will be described elsewhere<sup>25</sup>.

AC and cyclic voltammetry for a manganese  $T(p\text{-NH}_2)_2\text{PP}$  electrode is shown in Figure 3, cyclic voltammetry for iron  $T(p\text{-NH}_2)_2\text{PP}$  in Figure 4. Peak definition is presently inferior to that of the other metalloporphyrins due both to lower attained coverage and poorer background current.

We find no prior reports of electrochemistry of manganese tetraphenylporphyrin complexes in DMSO and must assume (we think reasonably)

that the two waves shown for the manganese  $T(p\text{-NH}_2)\text{PP}$  electrode in Figure 3 correspond to  $\text{Mn(III,II)}$  and porphyrin ring reductions. Potentials are given in Table I. The metal-centered reaction yields a smaller AC voltammetry wave than the ring reaction. The  $\text{Mn(III,II)}$  surface wave upon cyclic voltammetric examination interestingly is not as well resolved and often lies a few mv more negative on the virgin potential scan than is thereafter the case, as shown in the figure. We believe this illustrates the difference in coordination chemistry of the synthetic reaction pot and that of the electrochemical cell. The synthesized surface is probably initially in the  $\text{Mn(III)}T(p\text{-NH}_2)\text{PP}$  state, with acetate or other adventitious axial ligand. Upon electrochemical reduction these ligands are irreversibly lost by diffusion, and thereafter replaced upon metal reoxidation by solvent plus any other ligand added to the electrochemical medium.

Besides coordination with chloride (detectable with XPES) and adventitious ligand, the possibility of  $\mu$ -oxo dimer formation exists during or after surface metallation with manganese or iron. Electrochemical properties of the manganese  $\mu$ -oxo tetraphenylporphyrin are unknown, but iron  $\mu$ -oxo tetraphenylporphyrin has been reported in  $\text{DMF}^{24}$  to exhibit reduction at ca. -1.0 volt. As shown in Figure 4, the main features of a carbon- $\text{FeT}(p\text{-NH}_2)\text{PP}$  electrode are the -0.15 and -1.18 volt waves which are of equal magnitude, zero  $\Delta E_p$ , and in agreement with the formal potential of the monomer solution analog. Carbon- $\text{FeT}(p\text{-NH}_2)\text{PP}$  electrodes in  $\text{DMSO}$  often show a small but noticeable irreversible wave at ca. -0.61 volts, which could be evidence of surface bound  $\mu$ -oxo dimer. The possibility of surface-bound monomer porphyrin forming a dimer when metallated raises interesting questions regarding the stereochemistry of

of the immobilized porphyrin. In order to form a dimer, porphyrin molecules would have to be bonded "edge on" rather than "face down". We are continuing to investigate these questions, and hope to report on them in the future.

The XPES spectrum of surface bound iron porphyrin shows a Fe 3p 3/2 peak at 711.5 e.v., consistent with the 711.0 e.v. (referenced to C at 285.0) measured for Fe(III)TPPCl<sup>26</sup>. The most likely counter-ion for the surface bound iron porphyrin would be chloride, from the FeCl<sub>2</sub> reagent. Fe 2p, Cl 2p, and N 1s XPES intensities, and sensitivities calculated from escape depth and cross-sections<sup>27</sup>, result in measured atom ratios for Fe:Cl:N of 2.4:1:8, instead of the ideal ratios of 1:1:8. Various oxides and chlorides of iron may precipitate on the surface during the iron insertion reaction.

The electrochemistry of carbon-FeT(p-NH<sub>2</sub>)PP electrodes in aqueous media in the presence of dioxygen was of special interest in light of the demonstrated<sup>28</sup> electrocatalytic properties of the solution analog Fe(II)tetra(4-N-methylpyridyl)porphyrin. Figure 5 shows voltammetric scans of the Fe(III,II) potential region for a FeT(p-NH<sub>2</sub>)PP electrode in degassed 0.1 M KCl/H<sub>2</sub>O. After a large initial cathodic peak, the Fe(III,II) surface wave stabilizes and remains unchanged for the tested potential cycles. If the electrode is removed from the solution and exposed to air or if oxygen is bubbled through the solution followed by degassing with N<sub>2</sub>, the pattern of a large initial cathodic wave followed by a smaller, stable pattern is repeated. This behavior is also observed in 1 N H<sub>2</sub>SO<sub>4</sub>/H<sub>2</sub>O as shown by Figure 6a. The Fe(III,II) wave is less distinct than in KCl solution on the second and subsequent cycles, but is clearly present above background and is persistent. (The electrode

surface is resistant to acid hydrolysis within the time span of the experiment). Clearly in these experiments dioxygen is being adsorbed by the electrode in some manner and is being reduced, in a consuming burst, when the iron (II) porphyrin state is electrochemically generated.

Figure 6b shows the effect of bubbling  $O_2$  through the  $H_2SO_4$  solution for a few seconds, thereafter maintaining the cell under  $N_2$ . The initial cathodic scan produces a peak 3.4X larger ( $6.0 \times 10^{-4}$  coul./ $cm^2$ ) than the initial one in degassed medium ( $1.8 \times 10^{-4}$  coul./ $cm^2$ ) (Figure 6a), and is 33 times larger than the second cathodic scan in degassed solution ( $1.8 \times 10^{-5}$  coul./ $cm^2$ ), which represents the actual  $FeT(p-NH_2)PP$  coverage. A cyclic voltammogram of an unmodified carbon electrode in the same solution (Figure 6b) shows the current for non-catalyzed dioxygen reduction, at this low solution concentration level, rises at a more negative potential than the  $Fe(III,II)$  porphyrin wave. Thus, the enhanced current observed represents a modified surface-catalyzed dioxygen reduction couple with the iron porphyrin reaction having "turned over" a minimum of 33 times in these scans.

Unfortunately, this electrocatalytic activity is quite temporary. After about 10 to 20 scans, the observed current drops essentially to background. It is presently unknown whether the  $FeT(p-NH_2)PP$  has been rendered inactive by  $\mu$ -oxidimerization (unlikely in the acidic medium) or has been chemically degraded in some other possibly more permanent manner. Further work on this reaction is proceeding in order to examine the stability problem.

Electrochemistry of Protonated Tetraphenylporphyrin. The ring center of tetraphenylporphyrin (TPP) can accommodate uptake of two protons from

a strong acid. In investigations of protonated TPP NMR exchange rates<sup>29</sup>, and its molecular and crystal structure<sup>30</sup>, only the diacid, designated  $H_2TPP^{2+}$ , has been detected. Addition of a single proton to TPP is thought to distort the geometry of the porphyrin, promoting the addition of a second proton. Wilson, et al.<sup>31</sup> have studied the follow-up protonations of electroreduced porphyrins. No previous electrochemical studies of porphyrin protonated prior to reduction have been reported.

Using benzonitrile solvent for solubility reasons, we have titrated TPP with strong acids using cyclic voltammetry of the solutions as indicator. Figure 7 shows cyclic voltammetry of TPP before and after addition of two molar equivalents of  $HCLO_4$ . A small wave is present at -0.45 volt vs. NaSCE on the anodic potential scan after passage through the second (dianion) waves of TPP. A reversible wave grows at this potential upon  $HCLO_4$  addition, the TPP radical anion wave shrinks (proportionally), and the TPP radical dianion wave shrinks and becomes irreversible as well. This transformation is complete after two molar equivalents have been added; the solution at this point has also completed a transition from deep red-purple to deep green. The solution form at this point must be  $H_2TPP^{2+}$ , and the pair of closely overlapping waves at -0.45 volt represents the electrochemistry of this species.

Electroreduction of  $H_2TPP^{2+}$  necessarily is reduction of the porphyrin ring, and this reduction is obviously shifted strongly to positive potentials as compared to parent TPP. The  $H_2TPP^{2+}$  reduction of Figure 7 has in fact the most positive porphyrin ring reduction potential we know of. This is undoubtedly in part brought on by the positive charge of the species, although electronic effects associated with the ring distortion<sup>30</sup> must also be important. The  $H_2TPP^{2+}$  probably

does not bear the indicated full charge, in face, the dependency of the reduction potential of  $H_2TPP^{2+}$  in benzonitrile on the anion present indicates a substantial association effect. With nitrate as counter ion, the  $H_2TPP^{2+}$  wave shifts to -0.50 volt, and lies at -0.61 volt when chloride is used. The order of potentials is the same order as the dissociation tendencies of  $HClO_4$ ,  $HNO_3$ ,  $HCl$  in nitrile solvents<sup>32</sup>. Ogoshi, et al.<sup>33</sup> have reported the central hydrogens of protonated octaethylporphyrin are hydrogen bonded to the anions. It is probable that the splitting of the  $H_2TPP^{2+}$  reduction wave in Figure 7 involves such ion association effects rather than the monoprotonated  $HTPP^+$ , although this question was not explored in detail.

The connection of the above study with carbon bound  $T(p-NH_2)PP$  is traced to our observation<sup>2</sup> of an anodic wave at -0.4 volt vs. NaSCE following a potential scan in  $CH_3CN$  solvent through the dianion-producing wave of immobilized  $T(NH_2)PP$ . We have established that this wave is observable in DMSO as well, for carbon- $T(p-NH_2)PP$ , and for solution TPP as illustrated in Figure 7. We hypothesized that this new peak corresponded to oxidation of central ring-protonated porphyrin dianion sites. The proximity of the potentials observed for  $H_2TPP^{2+}$  electrochemistry to those of carbon- $T(p-NH_2)PP$  tend to substantiate this hypothesis. The proton source could be neighboring acidic sites on the carbon surface, as we theorized<sup>2</sup>, or trace water in the solvent.

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TABLE I

CYCLIC VOLTAMMETRY ELECTROCHEMISTRY RESULTS FOR CARBON BOUND TETRA(*p*-AMINOPHENYL)PORPHYRINS  
GLASSY CARBON, DMSO SOLVENT, 0.1 M  $\text{Et}_4\text{N}^+\text{ClO}_4^-$  ELECTROLYTE

Entry	Bound porphyrin	$E^{\circ}$ v. vs. NaSCe <sup>a</sup>			$E^{\circ}$ v. vs. SCE <sup>b</sup>	Remarks
		surf	Metal	Ring		
1	T( <i>p</i> -NH <sub>2</sub> )PP	-1.12±0.01	-	-1.51±0.01	2.9-14(Avg. 5.9)	-1.08, -1.45 c 6 samples
2	T( <i>p</i> -NH <sub>2</sub> )PP	-1.13±0.01	-	-1.52 0.01	1.0	-1.08, -1.45 c 2 samples, Prep. using $\text{CH}_3\text{COCl}$
3	T( <i>p</i> -NH <sub>2</sub> )PP	-1.15	-	0.5	-1.08, -1.45 c	No $\text{SOCl}_2$ or $\text{CH}_3\text{COCl}$
4	Cot( <i>p</i> -NH <sub>2</sub> )PP	-0.87	-	-1.99	-	-0.82, -1.87 c
5	Cut( <i>p</i> -NH <sub>2</sub> )PP	-	-	-1.21±0.01	-1.69±0.02	3.3-9.3 -1.20, -1.68 c 3 samples
6	Cut( <i>p</i> -NH <sub>2</sub> )PP	-	-	-1.26±0.01	-1.74±0.01	5.5 -1.20, -1.68 c 2 samples, Prep.
7	M1T( <i>p</i> -NH <sub>2</sub> )PP	-	-	-1.22±0.01	-1.80±0.01	4.8-5.5 -1.18, -1.75 c 2 samples
8	ZnT( <i>p</i> -NH <sub>2</sub> )PP	-	-	-1.42±0.03	-1.78±0.03	2.1-3.1 -1.31, -1.72 c 2 samples
9	MnT( <i>p</i> -NH <sub>2</sub> )PP	-0.30±0.01	-	-1.38±0.01	-	2.0 (-23, -1.38) d1 (-22, -1.31) d2 2 samples
10	Fet( <i>p</i> -NH <sub>2</sub> )PP	-0.15±0.02	-	-1.18±0.01	-	0.81 -0.11, -1.17, -1.68 e 2 samples
11	Fet( <i>p</i> -NH <sub>2</sub> )PP	-0.15	-	-	-	4.5 $\text{KCl}/\text{H}_2\text{O}$ solvent
12	Fet( <i>p</i> -NH <sub>2</sub> )PP	-0.12	-	-	-	1.6 $\text{H}_2\text{SO}_4/\text{H}_2\text{O}$ solvent

FOOTNOTES TO TABLE I

<sup>a</sup>From AC voltammetry peaks. Where cyclic voltammetry was also performed, the data are in agreement.

<sup>b</sup>Solution analog is tetraphenylporphyrin and corresponding metallated forms.

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### FIGURE LEGENDS

**Figure 1** Cyclic Voltammetry of C-T(p-NH<sub>2</sub>)PP in DMSO solvent with 0.1 M tetraethylammonium perchlorate; 100 mV/second,  $S = 38 \mu\text{A}/\text{cm}^2$ . Coverage from first reduction peak is  $1.4 \times 10^{-9} \text{ mole}/\text{cm}^2$ . Vertical lines show  $\Delta E_{\text{peak}} = 0$ .

**Figure 2.a.** Cyclic Voltammetry of carbon-CuT(p-NH<sub>2</sub>)PP in DMSO+0.1 M Et<sub>4</sub>N<sup>+</sup>ClO<sub>4</sub><sup>-</sup>. Sweep rate, 100 mV/sec., (—)Copper inserted from CuCl<sub>2</sub>·2H<sub>2</sub>O in refluxing DMF,  $S = 38 \mu\text{A}/\text{cm}^2$ . (----) Copper inserted from copper wire in DMSO,  $S = 19 \mu\text{A}/\text{cm}^2$ .

**Figure 2.b.** A.C. Voltammetry of (—)Carbon-NiT(p-NH<sub>2</sub>)PP, (---)Carbon-CuT(p-NH<sub>2</sub>)PP, and (-.-.)Carbon-ZnT(p-NH<sub>2</sub>)PP in DMSO+0.1 M Et<sub>4</sub>N<sup>+</sup>ClO<sub>4</sub><sup>-</sup>. Sweep rate, 2 mV/sec., 37 Hz AC signals applied at 2 mV RMS, 90° phase detection,  $S = 19 \mu\text{A}/\text{cm}^2$ .

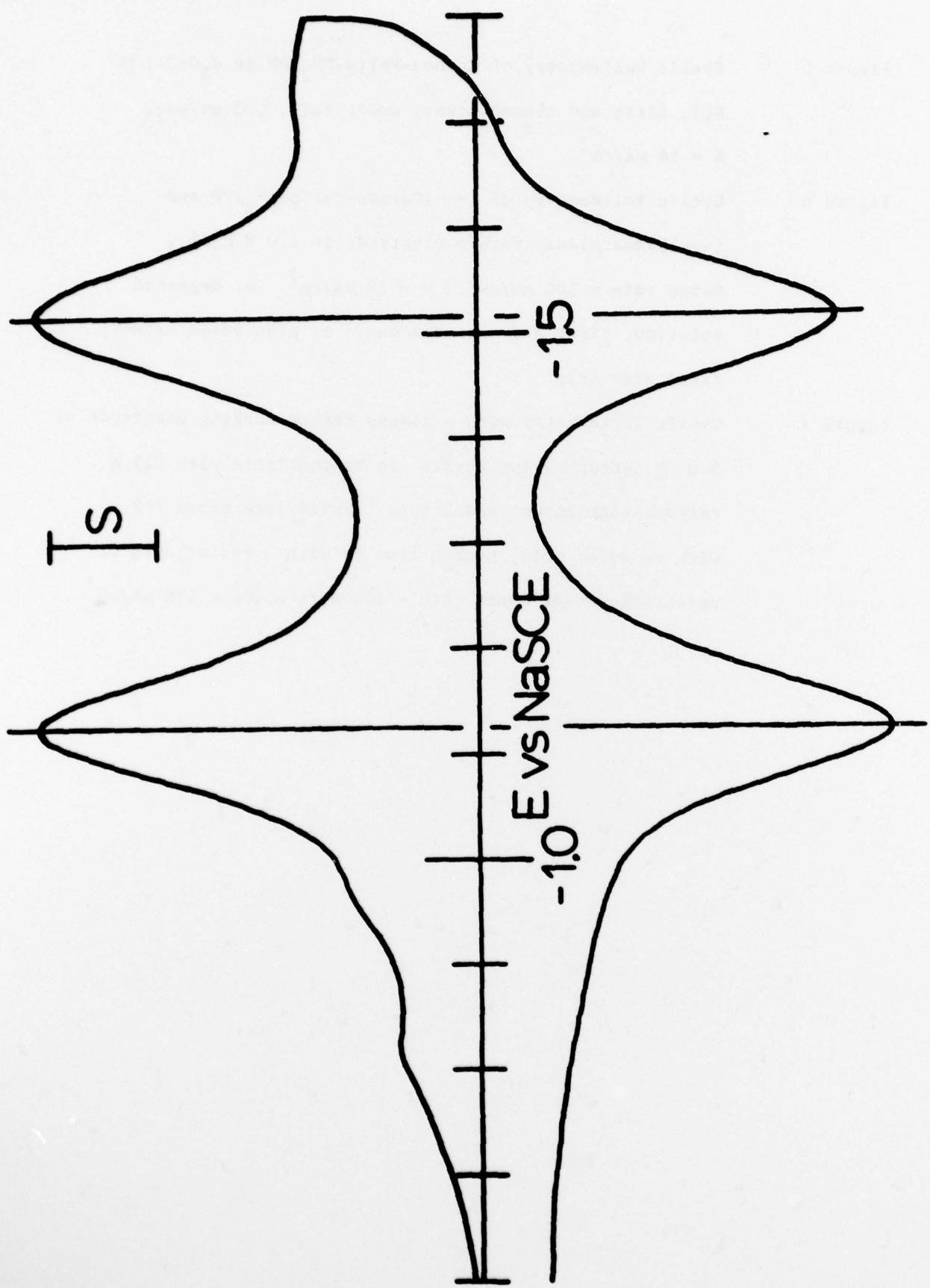
**Figure 3** Cyclic Voltammetry of Mn(III,II) reduction and A.C. Voltammetry of Carbon-MnT(p-NH<sub>2</sub>)PP in DMSO+0.1 M Et<sub>4</sub>N<sup>+</sup>ClO<sub>4</sub><sup>-</sup>. 0.6 volt section of cyclic voltammetry shows first scan, taken immediately after the electrode was removed from the DMF wash following Mn insertion. The second scan immediately followed the first. For C.V., sweep rate = 100 mV/sec.,  $S = 19 \mu\text{A}/\text{cm}^2$ . A.C. Voltammetry of 1.7 volt section employed 37 Hz signal applied at 2 mV RMS, 90° phase detection, sweep rate = 5 mV/sec.,  $S = 7.5 \mu\text{A}/\text{cm}^2$ .

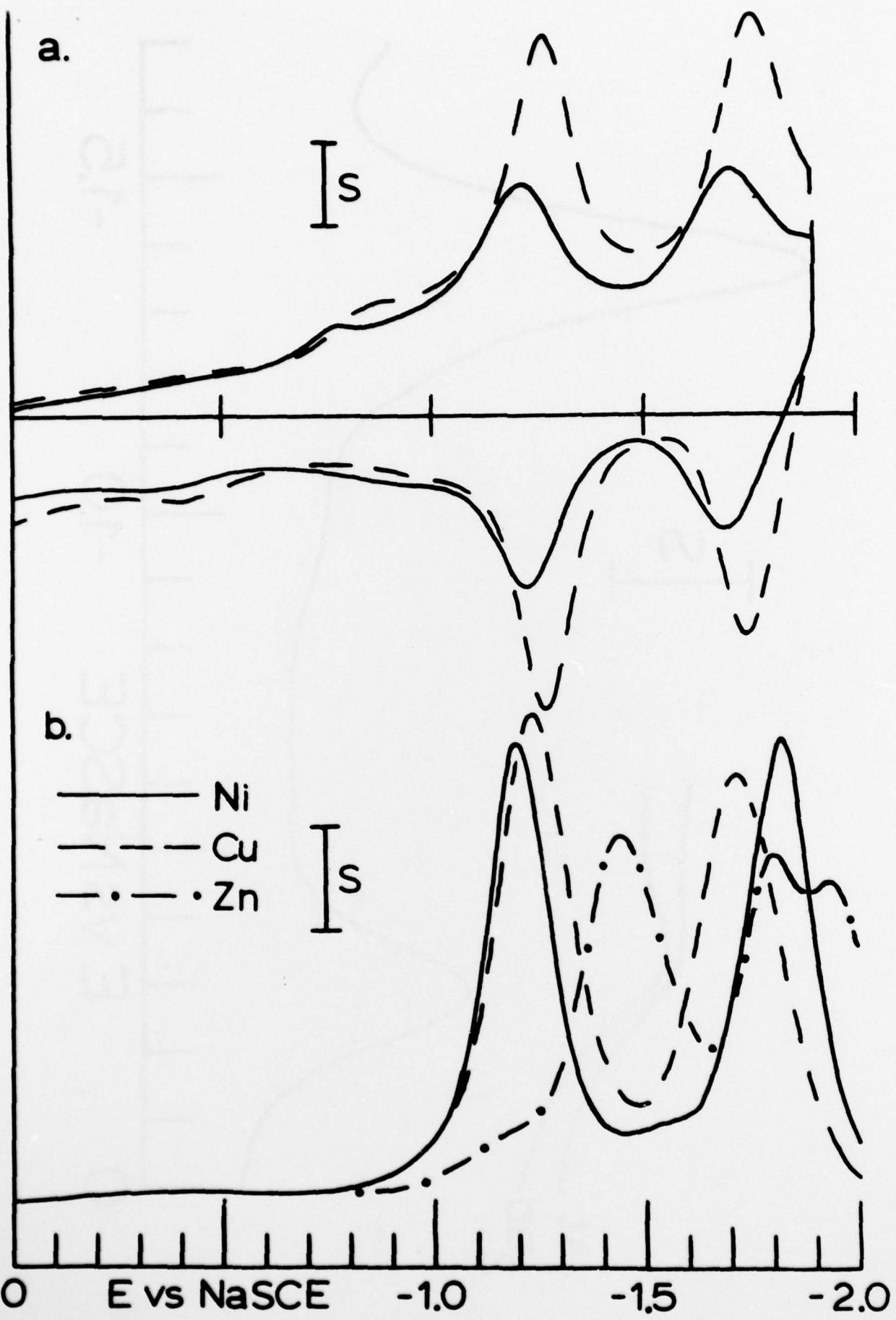
**Figure 4** Cyclic Voltammetry of C-FeT(p-NH<sub>2</sub>)PP in DMSO+0.1 M tetraethylammonium perchlorate. Sweep rate: 100 mV/sec,  $S = 19 \mu\text{A}/\text{cm}^2$ . Coverage measured from Fe III/II reduction:  $8.2 \times 10^{-11} \text{ mole}/\text{cm}^2$ .

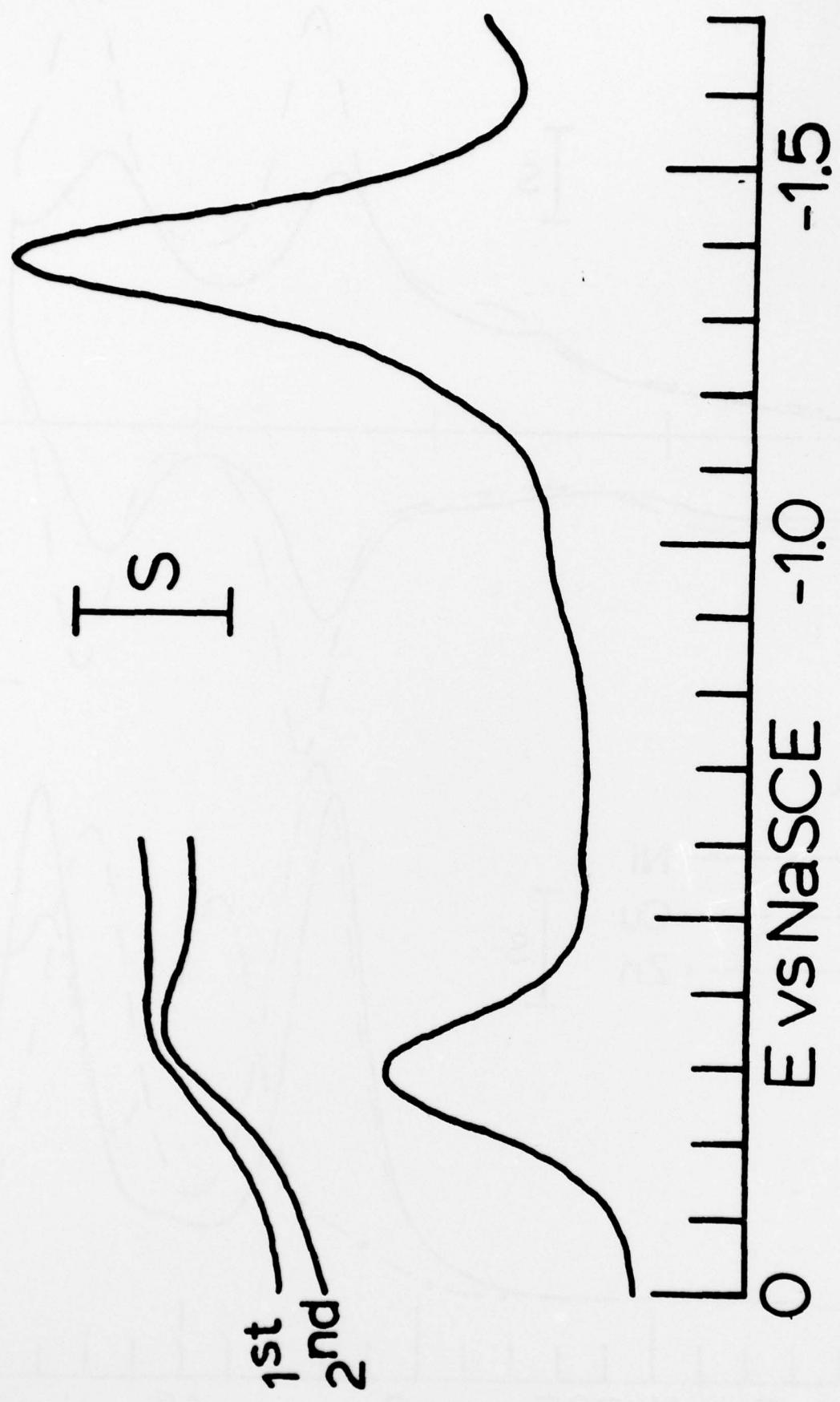
**Figure 5** Cyclic Voltammetry of Carbon-FeT(*p*-NH<sub>2</sub>)PP in H<sub>2</sub>O+0.1 M KCl, first and second scans; sweep rate, 100 mV/sec., S = 14  $\mu$ A/cm<sup>2</sup>.

**Figure 6** Cyclic Voltammetry of (—)Carbon-FeT(*p*-NH<sub>2</sub>)PP and (---)blank glassy carbon electrode in 1.0 N H<sub>2</sub>SO<sub>4</sub>, Sweep rate = 100 mV/sec., S = 38  $\mu$ A/cm<sup>2</sup>. a. degassed solution, first and second scans. b. plus added oxygen, first scan only.

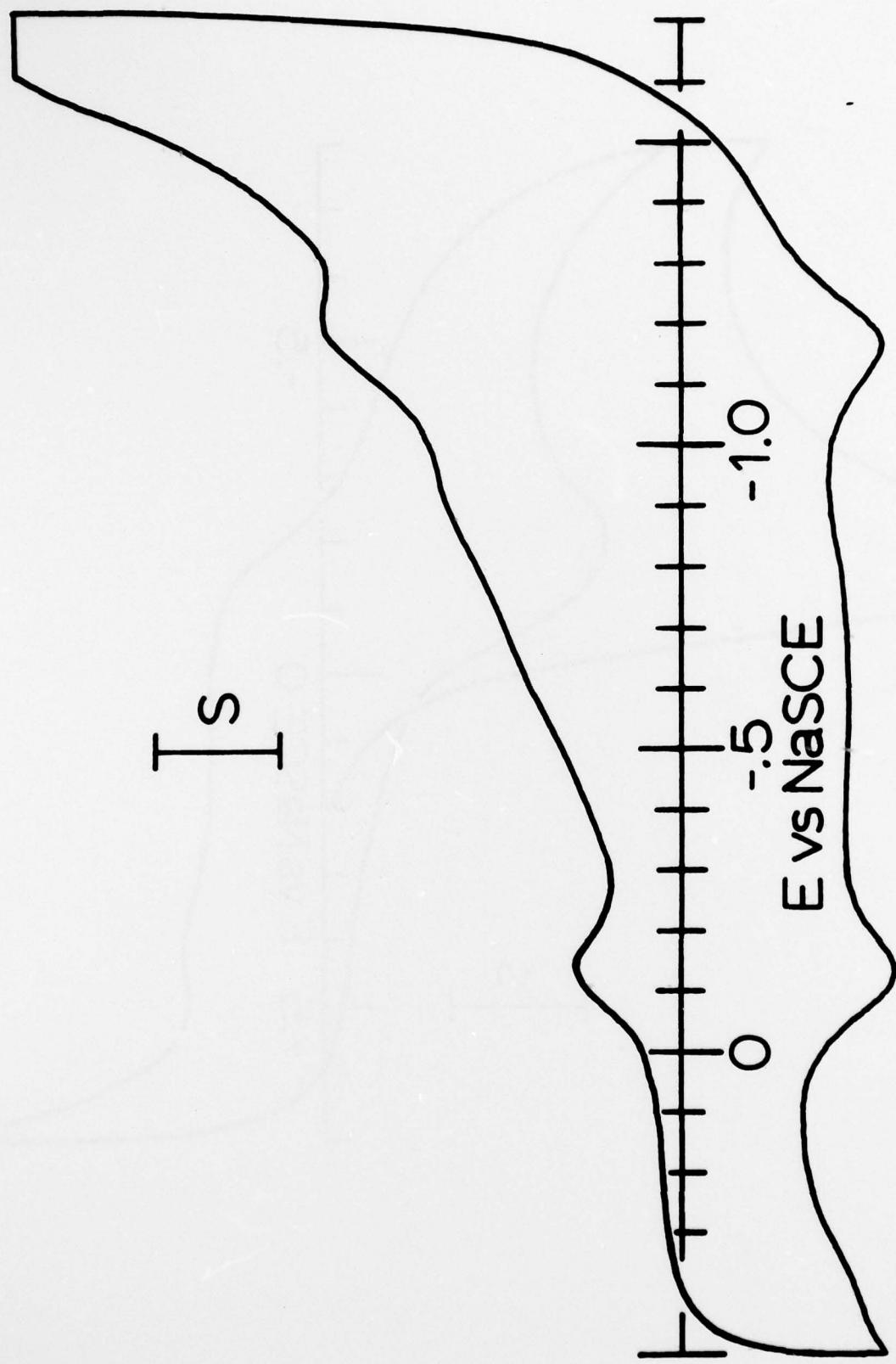
**Figure 7** Cyclic Voltammetry with a glassy carbon working electrode of 5.0 M tetrphenylporphyrin in benzonitrile with 0.1 M tetraethylammonium perchlorate. Solid line shows TPP with no added acid, broken line is with 2 equivalents of perchloric acid. Sweep rate = 100 mV/sec., S = 190  $\mu$ A/cm<sup>2</sup>.

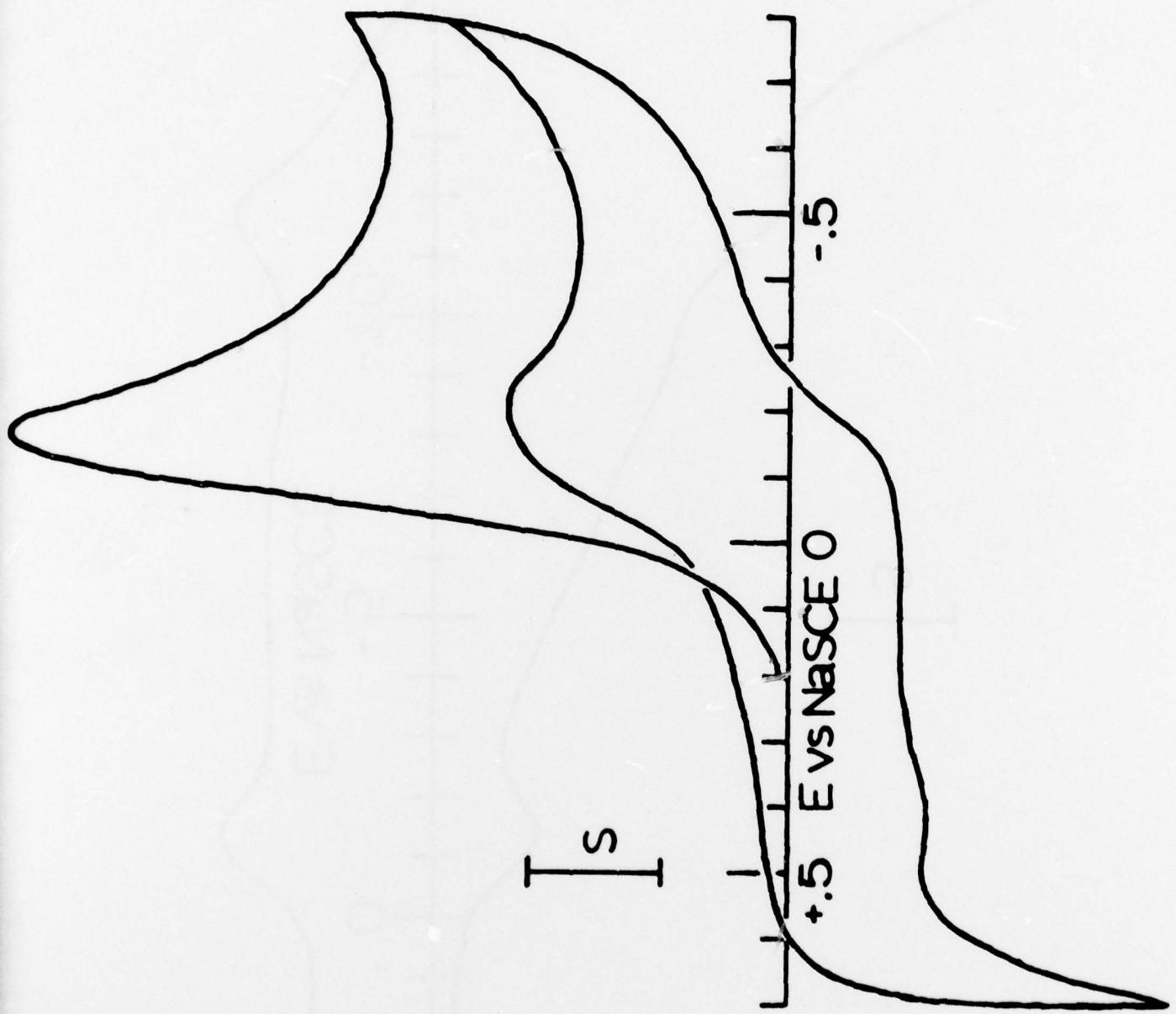


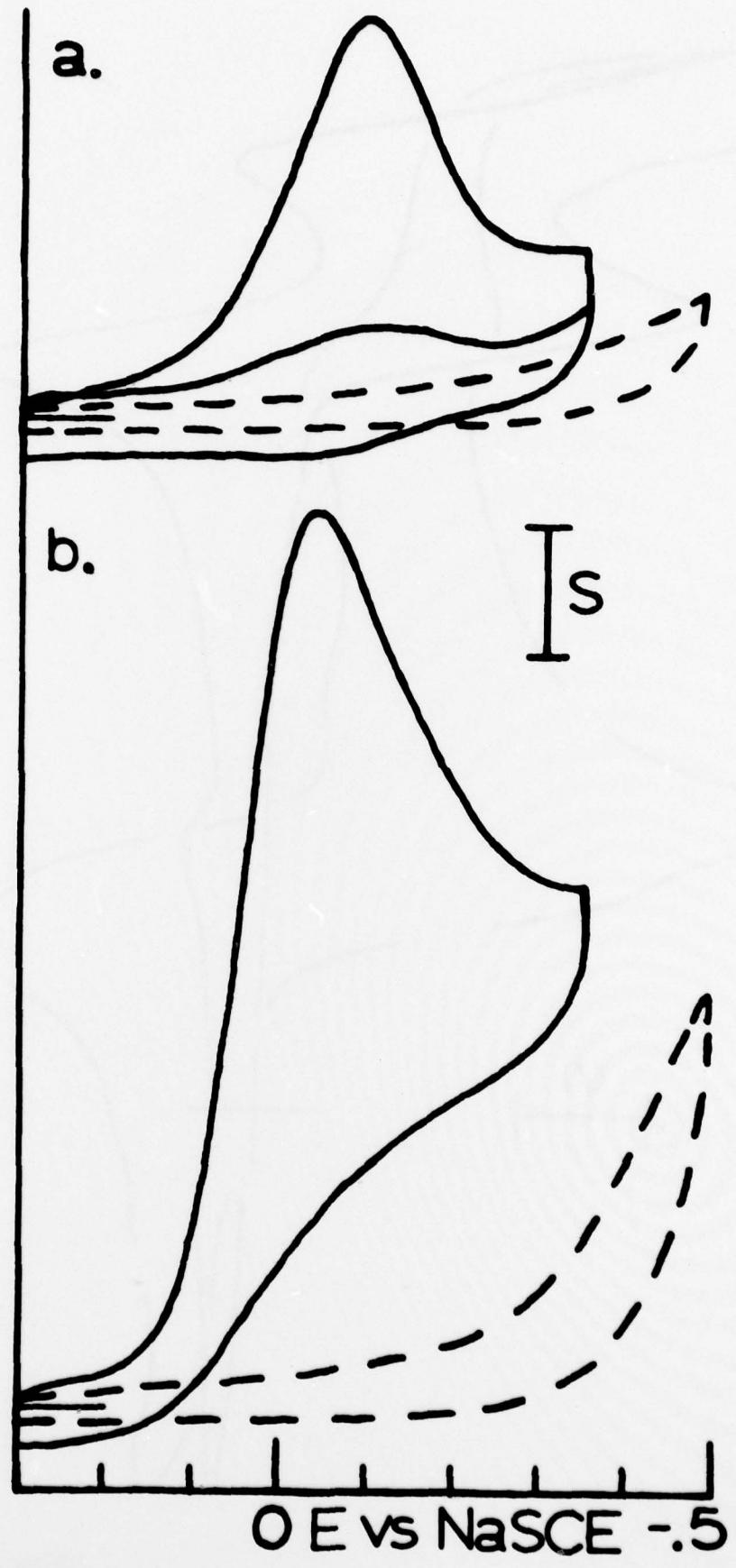


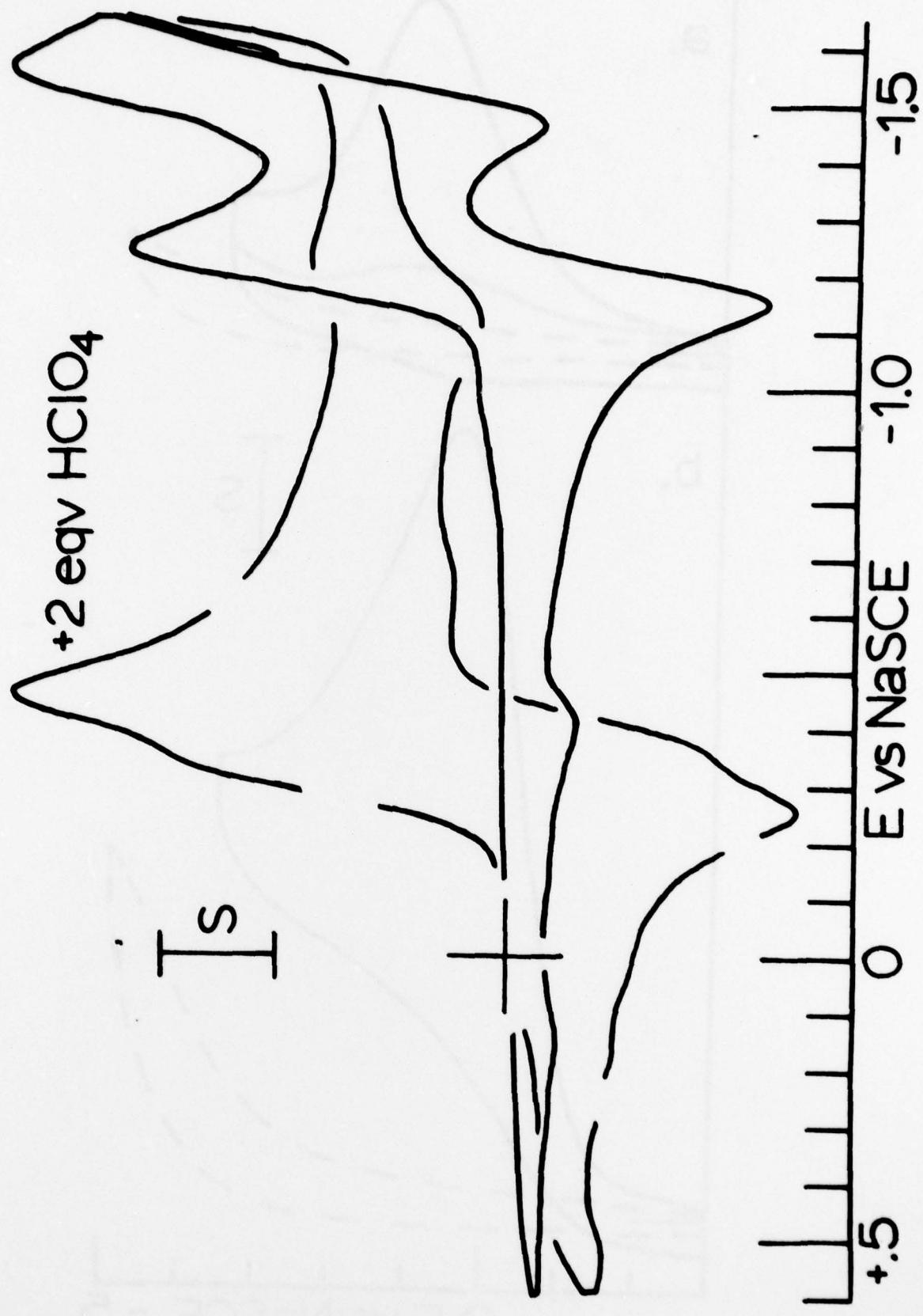


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